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1 **Manuscript**

2 **Chemical oxidation of dissolved organic matter by chlorine dioxide,**
3 **chlorine, and ozone: Effects on its optical and antioxidant properties**

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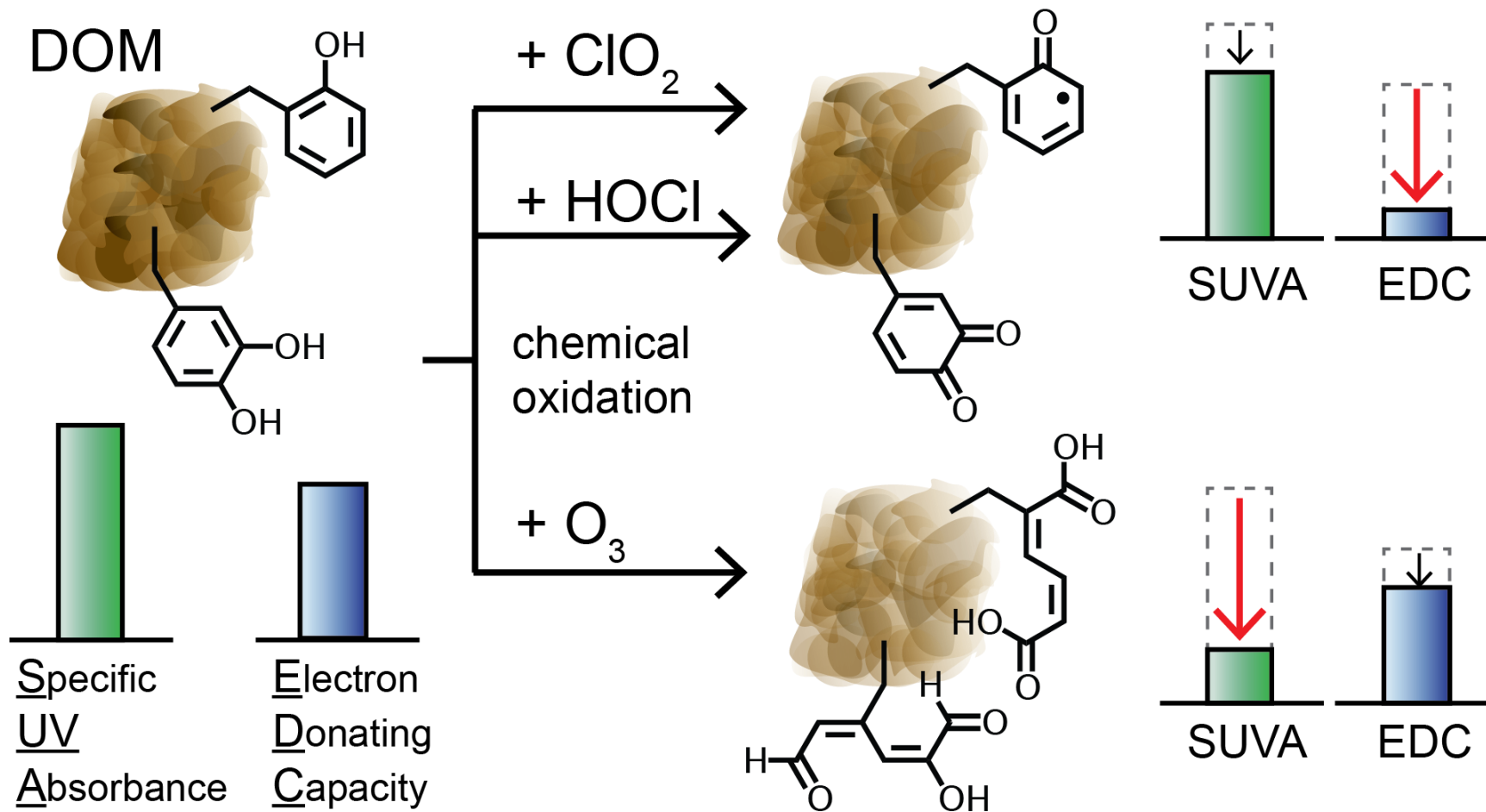
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Abstract

In water treatment dissolved organic matter (DOM) is typically the major sink for chemical oxidants. The resulting changes in DOM, such as its optical properties have been measured to follow the oxidation processes. However, such measurements contain only limited information on the changes in the oxidation states of and the reactive moieties in the DOM. In this study, we used mediated electrochemical oxidation to quantify changes in the electron donating capacities (EDCs), and hence the redox states, of three different types of DOM during oxidation with chlorine dioxide (ClO_2), chlorine (as HOCl/OCl^-), and ozone (O_3). Treatment with ClO_2 and HOCl resulted in comparable and prominent decreases in EDCs, while the UV absorbances of the DOM decreased only slightly. Conversely, ozonation resulted in only small decreases of the EDCs but pronounced absorbance losses of the DOM. These results suggest that ClO_2 and HOCl primarily reacted as oxidants by accepting electrons from electron-rich phenolic and hydroquinone moieties in the DOM, while O_3 reacted via electrophilic addition to aromatic moieties, followed by ring cleavage. This study highlights the potential of combined EDC-UV measurements to monitor chemical oxidation of DOM, to assess the nature of the reactive moieties and to study the underlying reaction pathways.

Introduction

Drinking water and wastewater treatment facilities often have a chemical oxidation step for disinfection, the removal of organic micropollutants, color removal and taste and odor control. Among the most commonly used oxidants are chlorine dioxide (ClO_2), chlorine (as hypochlorous acid, HOCl and OCl^-), and ozone (O_3).¹ For a number of

reasons, the efficiency of the oxidation step and the quality of the treated water largely depend on the reaction of the chemical oxidant with dissolved organic matter (DOM). First, DOM is a major contributor to drinking water color, which negatively affects the acceptance of the water among consumers.² Second, the reaction of DOM with the chemical oxidants accelerates their consumption and, thus, may reduce the efficiency of the oxidation step for disinfection and micropollutant oxidation.^{3,4} Third, the reaction of the oxidants with DOM may result in the formation of potentially harmful disinfection/oxidation by-products.⁵⁻⁷ Fourth, chemical DOM oxidation results in the generation of low molecular weight assimilable organic carbon (AOC)^{8,9}. Following the oxidation step, the AOC needs to be removed by biological filtration to improve the biological stability of drinking waters.^{4,10,11} For these reasons, information on the DOM concentration and its reactivity is indispensable to find the appropriate dose of an oxidant to meet the various requirements on oxidative water treatment processes and to avoid underperformance, higher costs, and undesired by-product formation during the oxidation step.

As a consequence, there is considerable interest in simple and readily measurable parameters that provide information on the concentration and reactivity of the DOM in the water.^{12,13} Two commonly measured parameters are the dissolved organic carbon (DOC) content, which captures the concentration of DOM, and the specific UV absorbance of the water at the wavelength of 254 nm ($SUVA_{254}$, expressed in $L\ mgC^{-1}\ m^{-1}$), which is a proxy for DOM aromaticity.¹⁴ Previous work showed that both the consumption of chemical oxidants by DOM and the occurrence of some disinfection/oxidation by-products are positively correlated to $SUVA_{254}$.¹⁵⁻¹⁹ These

correlations suggest activated aromatic moieties as major oxidizable functional groups in DOM, consistent with the high reactivity of low-molecular weight activated aromatic moieties, including phenols, methoxybenzenes and anilines, with ClO_2 , chlorine, and O_3 .²⁰⁻²⁹ However, despite the positive correlations with chemical oxidant consumption, SUVA_{254} alone was found to be a relatively poor predictor of DOM reactivity and disinfection byproduct formation with chlorine.^{14,30} Other methods that have been used to determine the concentration and reactivity of oxidizable moieties in DOM are difficult to adapt for routine water analysis or provide only indirect information on the redox states of DOM.³¹⁻³⁷ Therefore, an analytical method is desirable that allows for a direct quantification of changes in DOM oxidation states caused by reaction with chemical oxidants.³⁸

Mediated electrochemical oxidation (MEO), an analytical technique recently developed in our research group, fulfills these requirements. MEO allows for a fast and reliable quantification of the electron donating capacities (EDC) (i.e., the number of electrons that are donated by a given amount of DOM) of dilute DOM samples in electrochemical cells with well-controlled pH and E_h conditions.^{39,40} We previously demonstrated that MEO quantifies activated phenolic moieties in DOM: EDC values of a set of chemically diverse humic substances (HS) were positively correlated with their titrated phenol contents and showed dependencies on E_h and pH comparable to those of low molecular weight phenols and hydroquinones.⁴⁰ We expect that chemical oxidants oxidize these activated phenolic moieties in DOM, resulting in decreasing EDC values of the DOM during treatment. MEO may therefore be a powerful technique to quantify

DOM reactivity with chemical oxidants and to directly monitor changes in DOM oxidation states during chemical oxidation in water treatment.

The goal of this study was to explore the potential of combined MEO and UV-visible absorbance measurements to selectively quantify the oxidation states of DOM during chemical oxidation and to elucidate the underlying oxidant-dependent reaction pathways. We measured the UV-vis absorbance spectra and the EDC values of three HS (Suwannee River Humic and Fulvic Acids (SRHA and SRFA) and Pony Lake Fulvic Acid (PLFA)) during dose-dependent treatment with ClO_2 , chlorine, and O_3 . HS, in general, make up the major fraction of DOM. We specifically chose SRHA, SRFA, and PLFA because these materials are commercially available and have been used in previous oxidation studies,^{18,41} and their key physicochemical properties are known. Furthermore, SRHA/FA and PLFA represent allochthonous and autochthonous aquatic HS with terrestrial higher plant-derived and with microbially-derived precursor materials, respectively. This study addresses fundamental questions on the changes in DOM antioxidant properties and reactivities during chemical oxidation, and, in the implication section, highlights the potential of combining MEO and SUVA_{254} measurements to monitor chemical oxidant demand in water treatment facilities.

Materials and Methods

Chemicals. All chemicals were from commercial sources and used as received: *tert*-butanol (t-BuOH) ($\geq 99.7\%$), 2,2'-azino-bis(3-ethylbenzthiazoline-6-sulfonic acid) diammonium salt (ABTS) ($>99\%$), potassium peroxodisulfate ($\geq 99\%$), sodium chlorite (NaClO_2) (puriss. p.a. 80%), sodium chlorate (NaClO_3) ($\geq 99\%$), ortho-phosphoric acid (85%), sodium dihydrogen phosphate dihydrate ($\geq 99\%$), disodium hydrogen phosphate

dodecahydrate ($\geq 98.0\%$) and hypochlorite solution 6-14% were from Sigma-Aldrich, sodium dihydrogen phosphate monohydrate (99–102%) was from Merck.

Humic substances. Suwannee River Humic Acid Standard II (SRHA; catalogue number: 2S101H), Suwannee River Fulvic Acid Standard II (SRFA; 2S101F), and Pony Lake Fulvic Acid Reference (PLFA; 1R109F) were obtained from the International Humic Substances Society (IHSS, St. Paul, MN) and used as received. Selected physicochemical properties of the HS, including elemental compositions, aromaticities and phenol contents, are provided in **Table S1** in the Supporting Information.

Preparation of aqueous solutions. Aqueous solutions were prepared using deionized water either from Milli-Q (Millipore) or Barnsteadt water purification systems. HS stock solutions (100 mg C L^{-1}) were prepared in 5 mM phosphate buffer (pH 8) or in deionized water. The DOC of the HS stock solutions was determined after 25-fold dilution on a Shimadzu V-CPH TOC analyzer (Kyoto, Japan) and used to calculate SUVA_{254} and carbon-normalized EDC values.

Chlorine dioxide (ClO_2) stock solutions ($\sim 10 \text{ mM}$) were produced by mixing potassium peroxodisulfate ($\text{K}_2\text{S}_2\text{O}_8$, 2 g in 50 mL water) with sodium chlorite (NaClO_2 , 4 g in 50 mL).⁴² The stock solution of chlorine (Cl_2 ; $\sim 10 \text{ mM}$) was prepared by diluting a sodium hypochlorite solution with water. Ozone (O_3) stock solutions (~ 1.3 to 1.5 mM) were prepared by sparging ozone gas through water cooled in an ice bath.⁴³ The O_3 gas was formed from pure oxygen with an Apaco CMG 3-3 ozone generator (Grellingen, Switzerland). The exact concentrations of oxidants in the stock solutions were quantified spectrophotometrically using molar absorption coefficients of $\varepsilon = 1200 \text{ M}^{-1} \text{ cm}^{-1}$ at $\lambda =$

359 nm for ClO_2 ,⁴⁴ $\epsilon = 350 \text{ M}^{-1} \text{ cm}^{-1}$ at $\lambda = 290 \text{ nm}$ for chlorine (as ClO^-),⁴⁵ and $\epsilon = 3000 \text{ M}^{-1} \text{ cm}^{-1}$ at $\lambda = 258 \text{ nm}$ for ozone.⁴⁶

ClO_2 , chlorine, and O_3 oxidation of DOM. Oxidation experiments were carried out in a series of identical glass reaction vessels (50 or 100 mL) (Schott, Germany). The vessels contained either DOM solutions (nominal concentrations of $0.83 \text{ mmol C L}^{-1}$ (=10 mg C L^{-1}) after reagent mixing) or DOM-free blank solutions at pH 7 (50 mM phosphate buffer). Oxidant stock solutions were added to the vessels under vigorous mixing on a magnetic stirrer plate. The employed oxidant doses were in the ranges of 0–0.36 mmol $\text{ClO}_2/\text{mmol C}$, 0–0.85 mmol chlorine/mmol C, and 0–1.12 mmol $\text{O}_3/\text{mmol C}$, which cover the ranges commonly used for water treatment.^{28,47,48} Ozonation experiments were performed in the presence (5 mM) and absence of t-BuOH as a scavenger for formed hydroxyl radicals ($\bullet\text{OH}$). After oxidant addition, the vessels were closed, removed from the stirrer and stored at 22°C for 12h for chlorine dioxide, 3d for chlorine, and 2h for ozone. Subsequently, un-reacted ClO_2 and O_3 were removed from the solution by gently purging with helium for 20 min. In selected experiments, residual chlorine (max. $0.5 \mu\text{M}$) was measured using the DPD colorimetric method.⁴² The ozone exposure in the DOM-containing systems in the presence and absence of t-BuOH was measured according to previously described methods.^{49,50} Control experiments in which t-BuOH was added to the solutions after depletion of ozone showed that t-BuOH did not affect UV-visible absorption and EDC measurements.

UV/visible light absorbance measurements. Absorbance spectra of untreated and oxidized HS were collected on Uvikon 940 (Kontron Instruments) or Varian Cary 100 (Agilent Technologies) spectrophotometers in quartz glass cuvettes (Hellma) (10 or 100

mm path lengths). All sample spectra were corrected for the spectrum of the HS-free phosphate buffer (pH 7). The carbon-specific absorption coefficients of untreated and treated HS, $a(\lambda)$ [L / (mg C · m)], were calculated according to eq. 1, where $A(\lambda)$ is the sample absorption at a given wavelength λ , b [m] is the path length, and C_{HS} [mg C / L] is the organic carbon concentration of the untreated HS.

$$a(\lambda) = \frac{A(\lambda)}{b \times C_{\text{HS}}} \quad \text{Eq. 1}$$

The values $a(254 \text{ nm})$ and $a(280 \text{ nm})$ are referred to as SUVA_{254} and SUVA_{280} , respectively.. The spectral slope coefficients of the HS absorbance spectra, S [1/nm], were obtained by nonlinear least-square fitting of DOM absorption data from $\lambda = 300$ to 600 nm with a single exponential decay function,⁵¹ where $a(\lambda_{\text{ref}})$ is the specific absorption coefficient at the reference wavelength of $\lambda_{\text{ref}} = 350 \text{ nm}$.⁵²

$$a(\lambda) = a(\lambda_{\text{ref}}) \times \exp\left(-S \times (\lambda - \lambda_{\text{ref}})\right) \quad \text{Eq. 2}$$

The parameter S describes the steepness of DOM absorbance spectra on a logarithmic scale: The relative decrease in absorbance with increasing wavelength becomes steeper as S increases. Changes in the spectral slopes were also determined over narrower wavelength ranges (i.e., from 275-295 nm, $S_{275-295}$, and from 350-385 nm, $S_{350-385}$) following the approach suggested by Helms and coworkers.⁵³ Data fitting and integrations were performed using Origin 8.0 software (OriginLab).

Quantification of electron donating capacities. EDC values of untreated and oxidant-treated HS solutions were quantified by MEO using 2,2'-azino-bis(3-

ethylbenzthiazoline-6-sulfonic acid) (ABTS) as electron transfer mediator.^{39,40} MEO measurements were conducted in an electrochemical cell containing a reticulated vitreous carbon working electrode (WE), a Pt counter electrode, and an Ag/AgCl reference electrode. The electrochemical cells were first filled with 60-65 mL of buffer solution (0.1 M KCl, 0.1 M phosphate, pH 7) and the WE was polarized to an oxidizing potential of $E_h = +0.725$ V vs. the Standard Hydrogen Electrode (SHE), controlled by a potentiostat (either an Autolab PG302 (EcoChemie B.V.) or a 630C instrument (CH Instruments)). A volume of 2 mL of an aqueous ABTS solution (5 mM) was added to the cell, resulting in an oxidative current peak due to the oxidation of ABTS to its radical cation $ABTS^{+\bullet}$ (standard reduction potential $E_h^0(ABTS^{+\bullet}/ABTS) = 0.68$ V vs. SHE⁵⁴). Upon attainment of redox equilibrium between $ABTS^{+\bullet}/ABTS$ and the WE (and hence stable current readings), HS samples (5-7 mL) were successively spiked to the cell. Oxidation of electron donating moieties in the added HS by $ABTS^{+\bullet}$ resulted in the formation of reduced ABTS, which was subsequently re-oxidized at the WE to $ABTS^{+\bullet}$ to re-establish redox equilibrium. The resulting oxidative current peak was integrated to yield the EDC values of the added HS:

$$EDC = \frac{\int_0^t \frac{I}{F} dt}{m_{HS}} \quad \text{Eq. 3}$$

where I [A] is the baseline-corrected current and F ($=96485$ s A/mol_e.) is the Faraday constant, and m_{HS} [mg_C or mmol_C] is the mass/amount of HS analyzed. Most HS samples were analyzed in triplicates and some in duplicates with $t = 50$ min between replicate analysis to ensure baseline-separation of individual current peaks.

Results and Discussion

Effects of oxidant treatments on DOM optical properties. The specific absorption coefficients of the untreated samples decreased in the order SRHA > SRFA > PLFA over the entire measured wavelength range from 220 to 600 nm (**Figures S1** and **S2**). The trend in the absorption coefficients follows the decrease in HS aromaticity⁵⁵ from 31% for SRHA to 22% for SRFA and 12% for PLFA (**Table S1**).⁵⁶ The absorbance spectrum of untreated SRHA extended further into the red than the spectra of both SRFA and PLFA, which is reflected by the smaller *S* values for SRHA than for SRFA and PLFA. Longer wavelength absorbance of HS has been ascribed to charge transfer complexes between electron donor and acceptor pairs in HS,^{55,57,58} which may be more abundant in HA than FA.

Treatment of the HS with all oxidants resulted in decreasing specific absorption coefficients at all collected wavelengths (**Figures 1a-c**) and increasing *S* values (**Figure 1d-f**) with increasing oxidant doses, consistent with previous reports.^{8,37,59,60} The absorbance spectra, the differential spectra, and the spectral slopes $S_{275-295}$ and $S_{350-385}$ of untreated and oxidant-treated HS are shown in **Figures S1** to **S5**. Overall, the decreases in the specific absorption coefficients suggest a decrease in aromaticity of the treated HS. The increase in *S* values with increasing oxidant dose indicates that moieties/complexes absorbing at longer wavelengths were preferentially removed and/or transformed into shorter wavelength-absorbing components. The increase in *S* and $S_{275-295}$ values with increasing oxidant doses may also reflect decreases in the average molecular weights of the DOM upon reaction with the chemical oxidants, as detailed in the Supporting Information. Consistent with previous observations,^{30,61} the differential spectra for HOCl

234 treated HS show a local maximum in absorption loss at around 270-272 nm, indicating a
235 selective removal of chromophores in this wavelength region by reaction with chlorine. A
236 similar maximum loss in absorbance around 270 nm was also observed for ClO₂-treated
237 PLFA. This feature was absent from the differential spectra of ClO₂-treated SRHA and
238 SRFA as well as of the O₃-treated SRHA, SRFA, and PLFA both in absence and presence
239 of t-BuOH.

240 A detailed analysis of the absorbance and differential absorbance spectra revealed
241 that ClO₂ and HOCl treatments had different effects on DOM optical properties than the
242 O₃ treatments. The SUVA₂₅₄ and SUVA₂₈₀ values of all three HS decreased linearly with
243 increasing doses of ClO₂ and HOCl and followed similar dose-dependencies for the two
244 oxidants (**Figures 1a-c** and **Figure S6**, respectively). ClO₂ and HOCl treatment of SRHA
245 and SRFA also resulted in comparable increases in *S* with increasing oxidant doses, while
246 PLFA showed larger increases in *S* upon treatment with ClO₂ than HOCl at the same
247 specific molar oxidant doses (**Figure 1d-f**). In comparison to the ClO₂ and HOCl
248 treatments, ozonation resulted in much larger decreases in the specific absorption
249 coefficients of the HS, both in the absence and presence of t-BuOH (**Figures 1a-c** and
250 **S6d-f**). The larger decreases in SUVA₂₅₄ and SUVA₂₈₀ upon treatment with O₃ than ClO₂
251 and HOCl at the same specific molar oxidant doses demonstrates that UV-light absorbing
252 aromatic moieties in the HS were more efficiently removed (or transformed to less
253 efficiently absorbing moieties) by O₃ than by both ClO₂ and HOCl. Note that narrower
254 dose ranges were used for ClO₂ and HOCl than for O₃ based on the effects of the three
255 oxidants on the antioxidant properties of the HS, as detailed below.

Ozonation in the presence of t-BuOH resulted in larger losses in HS absorbance at wavelengths > 315 nm and larger increases in S than in the absence of t-BuOH. These effects of t-BuOH can be ascribed to two factors. First, t-BuOH scavenges $\bullet\text{OH}$ which are formed by DOM–ozone reactions and which catalytically degrade O_3 .^{16,62} Quenching of $\bullet\text{OH}$ by t-BuOH therefore enhanced O_3 lifetimes and, hence, resulted in higher O_3 exposures of the HS. Enhanced O_3 exposure in the presence compared to the absence of t-BuOH was verified experimentally with PLFA solutions (see **Figures S3, S4**). Second, by scavenging $\bullet\text{OH}$, t-BuOH shifted the overall oxidation pathway from unselective, diffusion-controlled $\bullet\text{OH}$ additions, $\bullet\text{H}$ abstraction (and electron transfer reactions),⁶² to more selective, direct reactions of O_3 with moieties such as olefins, activated aromatics and amines in the DOM.⁶² The presence of t-BuOH therefore enhanced O_3 -reaction induced cleavage of light absorbing olefinic and aromatic systems,⁶³ resulting in larger changes in HS optical properties than in the absence of t-BuOH.

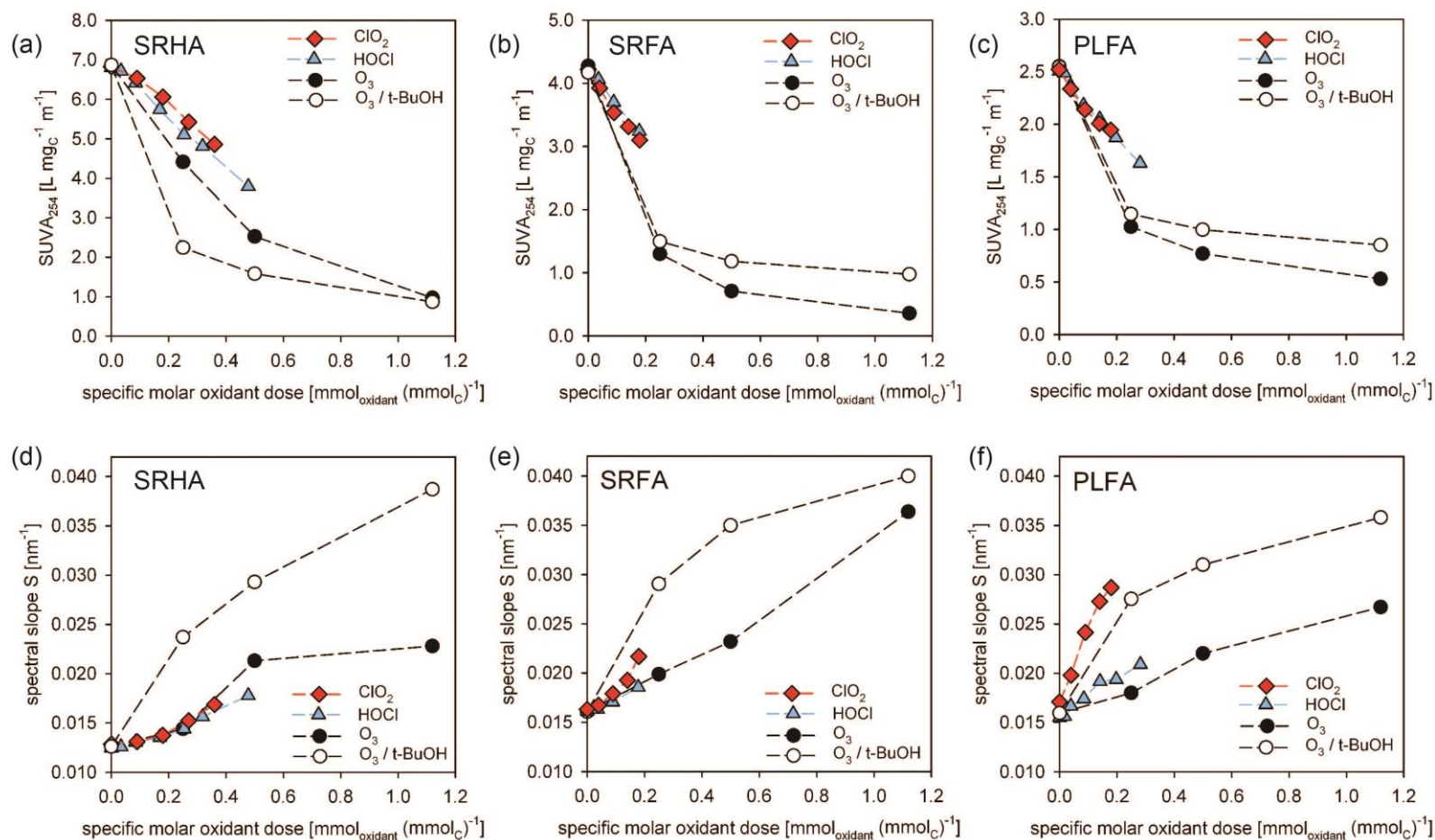


Figure 1. Changes in the optical properties of Suwannee River Humic Acid (SRHA), Suwannee River Fulvic Acid (SRFA), and Pony Lake Fulvic Acid (PLFA) upon treatment with chlorine dioxide (ClO_2), chlorine (as HOCl), and ozone (O_3) (both in the absence and presence of t-BuOH). Panels (a)-(c): Changes in the specific UV absorption at 254 nm (i.e., SUVA_{254}) of (a) SRHA, (b) SRFA, and (c) PLFA as a function of the specific molar oxidant dose ($\text{mmol}_{\text{oxidant}} (\text{mmol}_C)^{-1}$). Panels (d)-(f): Changes in the spectral slope S (from 300 to 600 nm) of (d) SRHA, (e) SRFA, and (f) PLFA as a function of the specific molar oxidant dose.

Effects of oxidant treatments on DOM antioxidant properties. In a first set of experiments we evaluated the sensitivity of MEO to detect oxidant-induced changes in the EDCs of HS by quantifying the kinetics of PLFA oxidation by O_3 at a constant initial dose of 0.5 mmol O_3 / mmol C. We chose PLFA because it has the lowest EDC values of several DOMs previously tested.⁴⁰ **Figure 2a** shows the evolution of the oxidative current responses in MEO for PLFA samples after reaction with O_3 for various times. The corresponding EDC values, obtained by integration of the oxidative current peaks (Eq. 3), show fast oxidation of the electron donating moieties in PLFA by O_3 (**Figure 2b**): Within one minute and 12 minutes of reaction, the EDC of PLFA decreased to approximately 50% and 15% of its original value, respectively. The results of this experiment demonstrate the suitability of MEO to quantify changes in the oxidation state of HS during treatments with chemical oxidants. Based on the reaction kinetics, the dose-dependent ozonation experiments were run for 2h to guarantee completion of HS- O_3 reactions.

Figure 3 shows that the EDCs of SRHA, SRFA, and PLFA decreased with increasing doses of ClO_2 , HOCl and O_3 (both in the presence and absence of t-BuOH) and, hence, dose-dependent removal of electron donating moieties in the HS for all three oxidants. Normalized to the same specific molar oxidant dose, the decreases in EDC were largest for ClO_2 , intermediate for HOCl and O_3 in the presence of t-BuOH, and smallest for O_3 in the absence of t-BuOH: Linear fits of the decreases in EDC values of SRHA and SRFA at low specific molar oxidant doses had the steepest slopes for ClO_2 (i.e., -0.69 and -0.46 mmol_e.(mmol ClO_2)⁻¹), intermediate slopes for HOCl (i.e., -0.38 and -0.36 mmol_e.(mmol HOCl)⁻¹) and for O_3 in the presence of t-BuOH (i.e., -0.35 and -0.29 mmol_e.(mmol

$\text{O}_3)^{-1}$), and the shallowest slopes for O_3 in the absence of t-BuOH (i.e., -0.15 and -0.08 $\text{mmol}_e\text{-(mmol O}_3)^{-1}$) (**Figure S5, Table S2**). The PLFA data did not show a linear decrease in EDC with increasing specific molar oxidant dose and could therefore not be fitted.

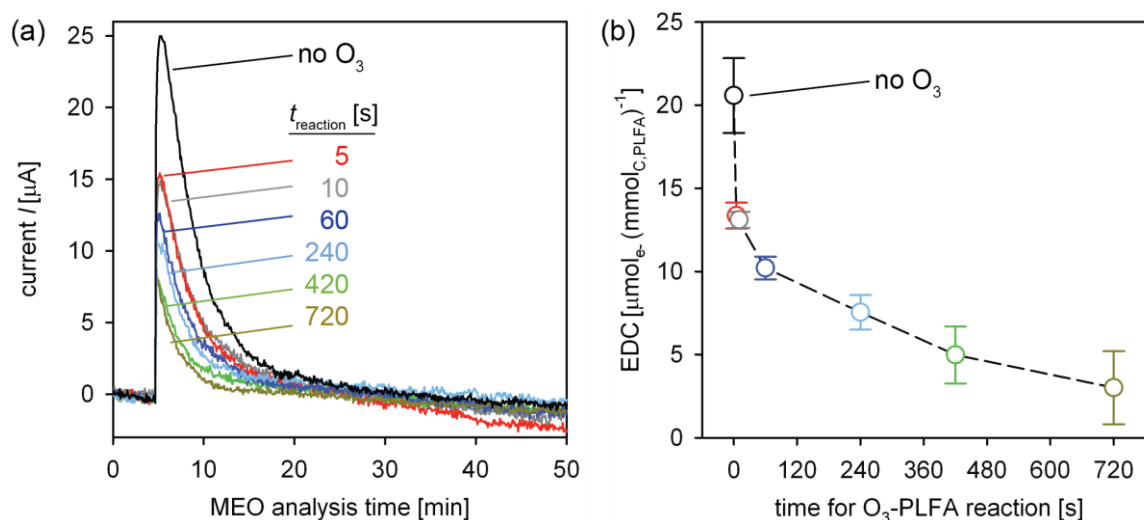
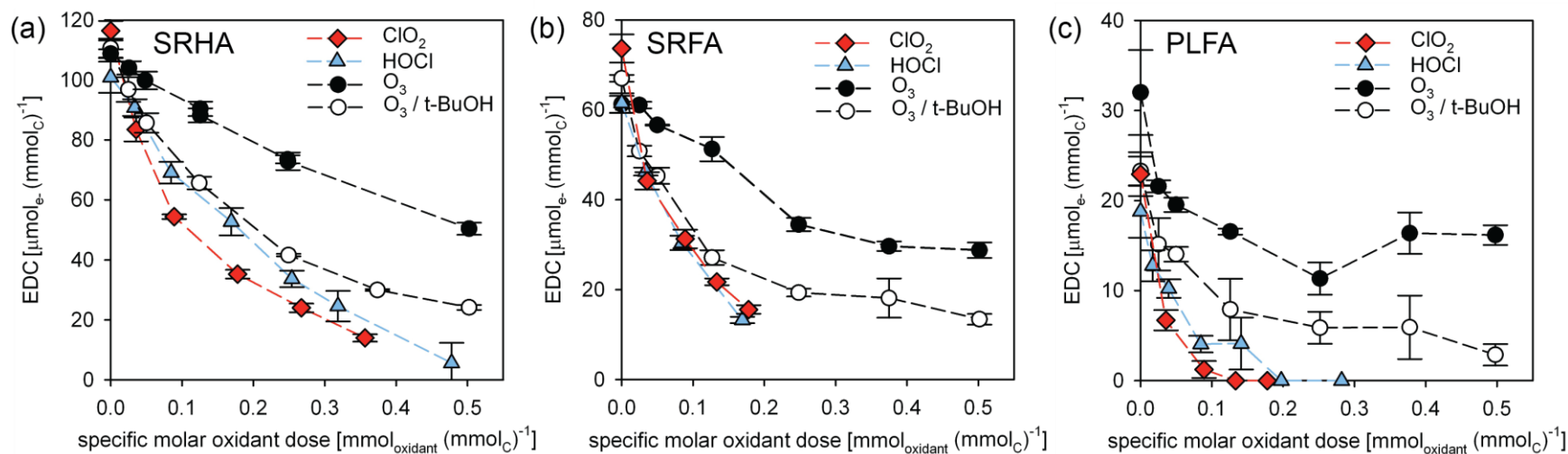


Figure 2. Ozonation of Pony Lake Fulvic Acid (PLFA). Effects of the reaction time on (a) the oxidative current responses in mediated electrochemical oxidation (MEO) and (b) the corresponding electron donating capacities (EDC) of PLFA. Experimental conditions: 0.5 $\text{mmol O}_3/\text{mmol C}$; 5 mM t-butanol; 50 mM PO_4 -buffer, pH 7.0. The samples were quenched with 1 mM maleic acid at selected reaction times.

Treatments with high doses of ClO_2 and HOCl resulted in complete loss of EDC in some of the systems, including a replicate SRFA- ClO_2 experiment (**Figure S6**), whereas all HS retained some EDC during ozonation even at the highest O_3 doses. The removal of electron-donating moieties in the tested HS was therefore more efficient by ClO_2 and HOCl treatments than by ozonation. The larger decreases in EDCs by O_3 in the presence than in the absence of t-BuOH can be assigned to $\bullet\text{OH}$ quenching by t-BuOH and hence higher O_3 exposures of HS and more selective oxidations of electron donating moieties by O_3 .



298

299 **Figure 3.** Dependencies of the electron donating capacities (EDCs) of (a) Suwannee River Humic Acid (SRHA), (b) Suwannee River
 300 Fulvic Acid (SRFA), and (c) Pony Lake Fulvic Acid (PLFA) on the specific molar doses of the chemical oxidants chlorine dioxide
 301 (ClO_2), chlorine (as HOCl), and ozone (in the absence and presence of t-BuOH).

Mechanistic interpretation. In the following, the changes in the optical and the antioxidant properties of the HS will be further explored by plotting the oxidant-induced decreases in the SUVA₂₅₄ values versus the corresponding decreases in the EDC values (**Figure 4**). Treatments of the HS with ClO₂ and HOCl resulted in comparable SUVA₂₅₄-EDC dependencies for these two oxidants with larger relative decreases in the EDC than in the SUVA₂₅₄ values. This finding implies a more efficient removal of electron donating phenolic moieties than UV-light absorbing aromatic moieties upon treatment of the HS with ClO₂ and HOCl. Compared to the ClO₂ and HOCl treatments, ozonation in the presence and absence of t-BuOH led to distinctly different SUVA₂₅₄-EDC dependencies with larger relative losses in the SUVA₂₅₄ than in the EDC values. Ozonation therefore caused a more efficient removal of UV-light absorbing aromatic moieties than electron donating phenolic moieties. Ozonation of SRHA in the presence and absence of t-BuOH resulted in comparable SUVA₂₅₄-EDC dependencies. Conversely, ozonation of SRFA in the presence of t-BuOH resulted in smaller decreases in SUVA₂₅₄ and larger decreases in the EDC values as compared to ozonation in the absence of t-BuOH at the same initial ozone dose. We note that the EDC measurements of PLFA samples at high O₃ doses were close to the quantification limit of MEO. The apparent increase in the EDC value of PLFA at the highest O₃ dose (**Figure 3c**) therefore likely reflected uncertainties in the EDC quantification.

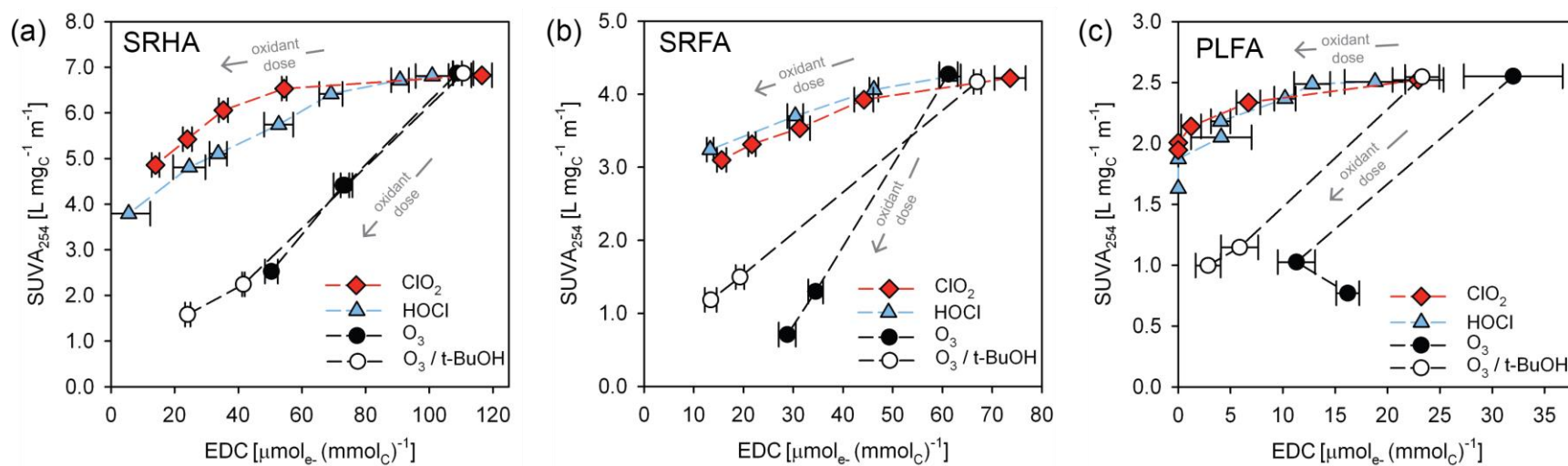


Figure 4. Effect of chemical oxidant treatments on the specific UV absorbances ($SUVA_{254}$) and the electron donating capacities (EDCs) of (a) Suwanee River Humic Acid (SRHA), (b) Suwanee River Fulvic Acid (SRFA), and (c) Pony Lake Fulvic Acid (PLFA). The chemical oxidants used were chlorine dioxide (ClO_2), chlorine (as $HOCl$), and ozone (O_3 ; in the absence and presence of tertiary butanol (t-BuOH)). The chemical oxidant dose increased in the direction indicated by the grey arrows.

The effects on the optical and antioxidant properties of the HS shown in **Figure 4** can be rationalized on the basis of known major reaction pathways of ClO_2 , HOCl , and O_3 with light-absorbing and electron donating phenolic moieties in the HS (**Figure 5**). ClO_2 reacts as a one-electron transfer oxidant with low molecular weight phenols forming chlorite and the corresponding phenoxyl radicals.²¹ At circumneutral pH, this reaction proceeds mostly via the phenolate species because of its oxidation rate constants with ClO_2 that are about six orders of magnitude higher than those for the non-dissociated phenol species.²⁶ Analogously to low molecular weight phenols, phenolic moieties in HS are expected to undergo one electron oxidation by ClO_2 . We have previously shown that HS contain electron donating phenolic and hydroquinone moieties with apparent oxidation potentials^{40,64} much lower than the standard reduction potential of ClO_2 , $E_h^0(\text{ClO}_{2(\text{aq})}/\text{ClO}_2^-) = 0.954 \text{ V}$.⁶⁵ SRHA and SRFA are derived from higher-plant precursor materials, including lignin, which is rich in methoxylated phenols.⁶⁶ Generally, methoxylation activates phenols for electrophilic attack and leads to faster oxidation kinetics.²⁶ Phenoxyl radicals resulting from a first one electron oxidation^{26,67,68} may either be further oxidized by reacting with another ClO_2 to form ortho- or para-quinones or undergo irreversible coupling reactions. Hydroquinone moieties present in the untreated HS are expected to be oxidized by ClO_2 to semiquinone intermediates and subsequently to the respective quinone moieties. These reaction pathways involving ClO_2 as the oxidant have in common that electron donating phenolic moieties are oxidized while their UV-light absorbing aromatic structure is preserved. In fact, based on the higher extinction coefficient of benzoquinone than hydroquinone at 254 nm, the oxidation of hydroquinone to quinone moieties in the DOM may have resulted in higher SUVA_{254} values than

measured if no hydroquinone moieties had been oxidized. These pathways are therefore fully consistent with the pronounced decreases in the EDC and the relatively small losses in SUVA₂₅₄ values observed for HS treatment with ClO₂.

Phenolic moieties in HS may react with HOCl in an electrophilic substitution reaction (**Figure 5**). At circumneutral pH, this reaction proceeds via the phenolate due to its much higher reactivity compared to the phenol.²⁸ In this reaction, HOCl attacks at the *ortho* and *para* positions to the hydroxyl substituent, resulting in the formation of (poly)-chlorinated phenols. Such an initial chlorination should not lead to a decrease in the electron donating capacities of the phenolic moieties.^{69,70} The reaction of low molecular weight phenols with HOCl has been demonstrated to proceed via polychlorinated phenols which ultimately undergo ring cleavage to form non-aromatic, chlorinated products (**Figure 5**).²⁸ However, the small changes in the SUVA₂₅₄ values of HS upon HOCl treatment do not support ring cleavage as a significant reaction pathway for phenolic, or more general, aromatic moieties present in HS. Alternatively, the smaller relative decreases in the SUVA₂₅₄ than EDC values upon HOCl treatment are consistent with the two-electron oxidation of hydroquinone and/or catechol moieties by HOCl to form the respective quinone moieties and chloride. These reactions are thermodynamically favorable given that the standard reduction potentials for the two electron reductions of HOCl and OCl⁻ (pK_a(HOCl)= 7.54 at 25°C) (i.e., HOCl + H⁺ + 2e⁻ → Cl⁻ + H₂O; E_h⁰= 1.48 V⁷¹ and OCl⁻ + H₂O + 2e⁻ → Cl⁻ + 2 OH⁻; E_h⁰= 0.84 V⁷¹) are much higher than the oxidation potentials of hydroquinones. This is in agreement with the high second order rate constants for the reaction of HOCl with hydroxyphenols.⁷² This reaction pathway

may therefore result in similar changes in the optical and antioxidant properties as ClO_2 , which acts almost exclusively by an electron transfer mechanism.

The reaction of phenolic moieties with O_3 at circumneutral pH is dominated by phenolate and initiated by an ozone adduct, which may react further by (i) loss of ozonide, O_3^- , to form a phenoxyl radical, (ii) loss of H_2O_2 to form an *ortho* benzoquinone, (iii) loss of singlet oxygen, $^1\text{O}_2$, to form a catechol-type compound, and (iv) a Criegee-type reaction with a cleavage of the aromatic ring.^{23,24,62} The formations of phenoxyl radicals (pathway (i)) and catechols (pathway (ii)) are important but minor pathways for the oxidation of phenol with ozone.²³ If these would be the dominant reaction pathways of phenolic moieties during ozonation, this would lead to comparatively large decreases in the EDC and small decreases in the SUVA_{254} values, while the opposite effect was observed experimentally (**Figure 4**). Instead, the pronounced decreases in SUVA_{254} support ring cleavage of phenols and hydroquinones via the Criegee mechanism (pathway (iv)) to form muconic-type compounds and eventually aliphatic aldehydes (**Figure 5**). Ring cleavage reactions may have involved non-phenolic aromatic moieties such as anisoles and polymethoxybenzenes, as demonstrated for low-molecular weight methoxylated compounds.²² The loss of these moieties would have resulted in decreasing SUVA_{254} without affecting the EDC values of the HS, as both the target compounds and products would not be oxidizable in MEO.

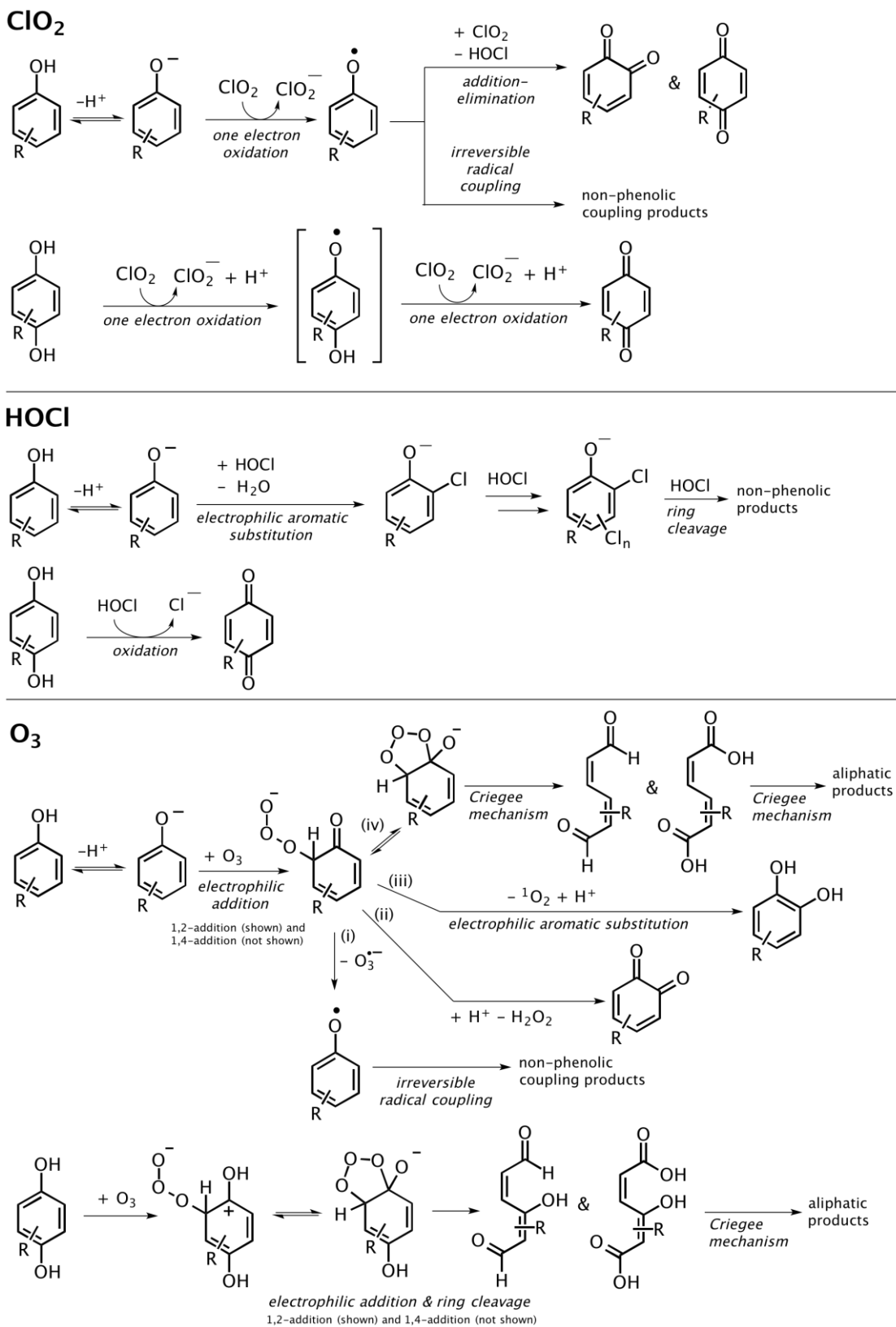


Figure 5. Proposed reaction pathways of phenolic moieties in the humic substances during reaction with chlorine dioxide (ClO₂), chlorine (HOCl), and ozone (O₃).

Implications

This study establishes that the EDC of DOM is a parameter that directly relates to the DOM redox state. The EDC is highly sensitive to changes in DOM occurring during chemical oxidation processes and can be readily quantified by mediated electrochemical oxidation (MEO). If combined with measurements of complementary optical parameters, such as SUVA₂₅₄, the changes in the EDC values provide information on the kinetics and the dose-dependent oxidation of electron donating moieties in DOM. The combined analysis of optical and antioxidant properties also provides insight into which moieties in the DOM react with the chemical oxidants and helps identifying the major oxidant-dependent reaction pathways of DOM.

In addition to advancing the fundamental understanding of chemical DOM oxidation, the results from this study are also relevant from a more applied, water treatment perspective. MEO has potential to be used in water treatment facilities to monitor DOM oxidation during a chemical oxidation step. Combined determination of changes in the EDC and SUVA₂₅₄ (or other suitable optical parameters) in close to real-time can be used to control chemical oxidant doses. The resulting refined dosing operation can minimize overdosing which may have negative impacts on water quality, such as the enhanced formation of disinfection/oxidation by-products. Future work needs to assess the potential of EDC-SUVA₂₅₄ measurements as a new tool to advance the understanding of and the capability to predict other important processes occurring during chemical oxidation of DOM, such as the formation of disinfection by-products, the generation of assimilable carbon, and the efficiency of disinfection.

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420 Supporting Information

421 This material is available free of charge via the internet at <http://pubs.acs.org>.

422 Literature Cited

- 423 1. Edzwald, J. K., *Water Quality & Treatment: A Handbook on Drinking Water*. 6th
424 ed.; McGraw-Hill Professional: New York, 2011.
- 425 2. Secondary Drinking Water Regulations: Guidance for Nuisance Chemicals, 816-
426 F-10-079. In Agency, U. S. E. P., Ed.
- 427 3. Wert, E. C.; Rosario-Ortiz, F. L.; Snyder, S. A.; Effect of ozone exposure on the
428 oxidation of trace organic contaminants in wastewater. *Water Research* **2009**, *43*, (4),
429 1005-1014.
- 430 4. von Gunten, U.; Ozonation of drinking water: Part I. Oxidation kinetics and
431 product formation. *Water Research* **2003**, *37*, (7), 1443-1467.
- 432 5. Richardson, S. D.; Plewa, M. J.; Wagner, E. D.; Schoeny, R.; DeMarini, D. M.;
433 Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-
434 products in drinking water: A review and roadmap for research. *Mutation Research-
435 Reviews in Mutation Research* **2007**, *636*, (1-3), 178-242.
- 436 6. Sedlak, D. L.; von Gunten, U.; The chlorine dilemma. *Science* **2011**, *331*, (6013),
437 42-43.
- 438 7. Lavonen, E. E.; Gonsier, M.; Tranvik, L. J.; Schmitt-Kopplin, P.; Köhler, S. J.;
439 Selective chlorination of natural organic matter - identification of previously unknown
440 disinfection by-products. *Environmental Science & Technology* **2013**, *47*, (5), 2264-2271.
- 441 8. Swietlik, J.; Dabrowska, A.; Raczyk-Stanislawiak, U.; Nawrocki, J.; Reactivity of
442 natural organic matter fractions with chlorine dioxide and ozone. *Water Research* **2004**,
443 *38*, (3), 547-558.
- 444 9. Ramseier, M. K.; Peter, A.; Traber, J.; von Gunten, U.; Formation of assimilable
445 organic carbon during oxidation of natural waters with ozone, chlorine dioxide, chlorine,
446 permanganate, and ferrate. *Water Research* **2011**, *45*, (5), 2002-2010.
- 447 10. Camel, V.; Bermond, A.; The use of ozone and associated oxidation processes in
448 drinking water treatment. *Water Research* **1998**, *32*, (11), 3208-3222.
- 449 11. Hammes, F.; Salhi, E.; Koster, O.; Kaiser, H. P.; Egli, T.; von Gunten, U.;
450 Mechanistic and kinetic evaluation of organic disinfection by-product and assimilable

- organic carbon (AOC) formation during the ozonation of drinking water. *Water Research* **2006**, *40*, (12), 2275-2286.
12. Bourgeois, W.; Burgess, J. E.; Stuetz, R. M.; On-line monitoring of wastewater quality: a review. *Journal of Chemical Technology and Biotechnology* **2001**, *76*, (4), 337-348.
13. Olsson, G.; ICA and me - A subjective review. *Water Research* **2012**, *46*, (6), 1585-1624.
14. Weishaar, J. L.; Aiken, G. R.; Bergamaschi, B. A.; Fram, M. S.; Fujii, R.; Mopper, K.; Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. *Environmental Science & Technology* **2003**, *37*, (20), 4702-4708.
15. Kitis, M.; Karanfil, T.; Wigton, A.; Kilduff, J. E.; Probing reactivity of dissolved organic matter for disinfection by-product formation using XAD-8 resin adsorption and ultrafiltration fractionation. *Water Research* **2002**, *36*, (15), 3834-3848.
16. Buffle, M. O.; Schumacher, J.; Meylan, S.; Jekel, M.; von Gunten, U.; Ozonation and advanced oxidation of wastewater: Effect of O₃ dose, pH, DOM and HO center dot scavengers on ozone decomposition and HO center dot generation. *Ozone-Science & Engineering* **2006**, *28*, (4), 247-259.
17. Westerhoff, P.; Aiken, G.; Amy, G.; Debroux, J.; Relationships between the structure of natural organic matter and its reactivity towards molecular ozone and hydroxyl radicals. *Water Research* **1999**, *33*, (10), 2265-2276.
18. Elovitz, M. S.; Von Gunten, U.; Kaiser, H., The influence of dissolved organic matter character on ozone decomposition rates and Rct. In *Natural Organic Matter and Disinfection By-Products: Characterization and Control in Drinking Water*, Barrett, S. E.; Krasner, S. W.; Amy, G. L., Eds. ACS Publications: 2000; Vol. 761, pp 248-269.
19. Reckhow, D. A.; Singer, P. C.; Malcolm, R. L.; Chlorination of humic materials: byproduct formation and chemical interpretations *Environmental Science & Technology* **1990**, *24*, (11), 1655-1664.
20. Hoigné, J.; Bader, H.; Rate constants of reactions of ozone with organic and inorganic compounds in water. 1. Non-dissociating organic compounds. *Water Research* **1983**, *17*, (2), 173-183.
21. Hoigné, J.; Bader, H.; Rate constants of reactions of ozone with organic and inorganic compounds in water. 2. Dissociating organic compounds. *Water Research* **1983**, *17*, (2), 185-194.
22. Mvula, E.; Naumov, S.; von Sonntag, C.; Ozonolysis of lignin models in aqueous solution: Anisole, 1,2-Dimethoxybenzene, 1,4-Dimethoxybenzene, and 1,3,5-Trimethoxybenzene. *Environmental Science & Technology* **2009**, *43*, (16), 6275-6282.
23. Mvula, E.; von Sonntag, C.; Ozonolysis of phenols in aqueous solution. *Organic & Biomolecular Chemistry* **2003**, *1*, (10), 1749-1756.
24. Ramseier, M. K.; von Gunten, U.; Mechanisms of phenol ozonation-kinetics of formation of primary and secondary reaction products. *Ozone-Science & Engineering* **2009**, *31*, (3), 201-215.
25. Singer, P. C.; Gurol, M. D.; Dynamics of the ozonation of phenol. 1. Experimental observations. *Water Research* **1983**, *17*, (9), 1163-1171.

26. Tratnyek, P. G.; Hoigné, J.; Kinetics of reactions of chlorine dioxide (OCIO) in water. 2. Quantitative structure activity relationships for phenolic compounds. *Water Research* **1994**, *28*, (1), 57-66.
27. Norwood, D. L.; Johnson, J. D.; Christman, R. F.; Hass, J. R.; Bobenrieth, M. J.; Reactions of chlorine with selected aromatic models of aquatic humic material. *Environmental Science & Technology* **1980**, *14*, (2), 187-190.
28. Gallard, H.; von Gunten, U.; Chlorination of phenols: Kinetics and formation of chloroform. *Environmental Science & Technology* **2002**, *36*, (5), 884-890.
29. Lee, Y.; von Gunten, U.; Oxidative transformation of micropollutants during municipal wastewater treatment: Comparison of kinetic aspects of selective (chlorine, chlorine dioxide, ferrate(VI), and ozone) and non-selective oxidants (hydroxyl radical). *Water Research* **2010**, *44*, (2), 555-566.
30. Li, C. W.; Benjamin, M. M.; Korshin, G. V.; The relationship between TOX formation and spectral changes accompanying chlorination of pre-concentrated or fractionated NOM. *Water Research* **2002**, *36*, (13), 3265-3272.
31. Abbt-Braun, G.; Lankes, U.; Frimmel, F. H.; Structural characterization of aquatic humic substances - The need for a multiple method approach. *Aquatic Sciences* **2004**, *66*, (2), 151-170.
32. Westerhoff, P.; Mezyk, S. P.; Cooper, W. J.; Minakata, D.; Electron pulse radiolysis determination of hydroxyl radical rate constants with Suwannee river fulvic acid and other dissolved organic matter isolates. *Environmental Science & Technology* **2007**, *41*, (13), 4640-4646.
33. Westerhoff, P.; Debroux, J.; Aiken, G.; Amy, G.; Ozone-induced changes in natural organic matter (NOM) structure. *Ozone-Science & Engineering* **1999**, *21*, (6), 551-570.
34. These, A.; Reemtsma, T.; Structure-dependent reactivity of low molecular weight fulvic acid molecules during ozonation. *Environmental Science & Technology* **2005**, *39*, (21), 8382-8387.
35. Pelekani, C.; Newcombe, G.; Snoeyink, V. L.; Hepplewhite, C.; Assemi, S.; Beckett, R.; Characterization of natural organic matter using high performance size exclusion chromatography. *Environmental Science & Technology* **1999**, *33*, (16), 2807-2813.
36. Collins, M. R.; Amy, G. L.; Steelink, C.; Molecular weight distribution, carboxylic acidity, and humic substance content of aquatic organic matter - Implications for removal during water treatment *Environmental Science & Technology* **1986**, *20*, (10), 1028-1032.
37. Korshin, G. V.; Benjamin, M. M.; Chang, H. S.; Gallard, H.; Examination of NOM chlorination reactions by conventional and stop-flow differential absorbance spectroscopy. *Environmental Science & Technology* **2007**, *41*, (8), 2776-2781.
38. Macalady, D. L.; Walton-Day, K., Redox Chemistry and Natural Organic Matter (NOM): Geochemists' Dream, Analytical Chemists' Nightmare. In *Aquatic Redox Chemistry*, Tratnyek, P. G.; Grundl, T. J.; Haderlein, S. B., Eds. American Chemical Society: Washington, 2011.
39. Aeschbacher, M.; Sander, M.; Schwarzenbach, R. P.; Novel electrochemical approach to assess the redox properties of humic substances. *Environmental Science & Technology* **2010**, *44*, (1), 87-93.

40. Aeschbacher, M.; Graf, C.; Schwarzenbach, R. P.; Sander, M.; Antioxidant properties of humic substances. *Environmental Science & Technology* **2012**, *46*, (9), 4916-4925.
41. Zhang, X. R.; Minear, R. A.; Barrett, S. E.; Characterization of high molecular weight disinfection byproducts from chlorination of humic substances with/without coagulation pretreatment using UF-SEC-ESI-MS/MS. *Environmental Science & Technology* **2005**, *39*, (4), 963-972.
42. Gates, D., *The chlorine dioxide handbook*. American Water Works Association: Denver, CO, 1998.
43. Bader, H.; Hoigné, J.; Determination of ozone in water by the indigo method. *Water Research* **1981**, *15*, (4), 449-456.
44. Hoigné, J.; Bader, H.; Kinetics of reactions of chlorine dioxide (OClO) in water. 1. Rate constants for inorganic and organic compounds. *Water Research* **1994**, *28*, (1), 45-55.
45. Soulard, M.; Bloc, F.; Hatterer, A.; Diagrams of existence of chloramines and bromamines in aqueous solution. *Journal of the Chemical Society-Dalton Transactions* **1981**, (12), 2300-2310.
46. Liu, Q.; Schurter, L. M.; Muller, C. E.; Aloisio, S.; Francisco, J. S.; Margerum, D. W.; Kinetics and mechanisms of aqueous ozone reactions with bromide, sulfite, hydrogen sulfite, iodide, and nitrite ions. *Inorganic Chemistry* **2001**, *40*, (17), 4436-4442.
47. Huber, M. M.; Korhonen, S.; Ternes, T. A.; von Gunten, U.; Oxidation of pharmaceuticals during water treatment with chlorine dioxide. *Water Research* **2005**, *39*, (15), 3607-3617.
48. Zimmermann, S. G.; Wittenwiler, M.; Hollender, J.; Krauss, M.; Ort, C.; Siegrist, H.; von Gunten, U.; Kinetic assessment and modeling of an ozonation step for full-scale municipal wastewater treatment: Micropollutant oxidation, by-product formation and disinfection. *Water Research* **2011**, *45*, (2), 605-617.
49. Hoigné, J.; Bader, H.; Characterization of water quality criteria for ozonation processes. 2. Lifetime of added ozone *Ozone-Science & Engineering* **1994**, *16*, (2), 121-134.
50. von Gunten, U.; Holgne, J.; Bromate formation during ozonation of bromide containing waters - interaction of ozone and hydroxyl radical reactions. *Environmental Science & Technology* **1994**, *28*, (7), 1234-1242.
51. Twardowski, M. S.; Boss, E.; Sullivan, J. M.; Donaghay, P. L.; Modeling the spectral shape of absorption by chromophoric dissolved organic matter. *Marine Chemistry* **2004**, *89*, (1-4), 69-88.
52. Golanoski, K. S.; Fang, S.; Del Vecchio, R.; Blough, N. V.; Investigating the mechanism of phenol photooxidation by humic substances. *Environmental Science & Technology* **2012**, *46*, (7), 3912-3920.
53. Helms, J. R.; Stubbins, A.; Ritchie, J. D.; Minor, E. C.; Kieber, D. J.; Mopper, K.; Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter. *Limnology and Oceanography* **2008**, *53*, (3), 955-969.
54. Scott, S. L.; Chen, W. J.; Bakac, A.; Espenson, J. H.; Spectroscopic parameters, electrode potentials, acid ionization constants, and electron exchange rates of the 2,2'-

- Azinobis(3-ethylbenzothiazoline-6-sulfonate) radicals and ions. *Journal of Physical Chemistry* **1993**, 97, (25), 6710-6714.
55. Chin, Y. P.; Aiken, G.; Oloughlin, E.; Molecular weight, polydispersity, and spectroscopic properties of aquatic humic substances. *Environmental Science & Technology* **1994**, 28, (11), 1853-1858.
56. Thorn, K. A.; Folan, D. W.; MacCarthy, P. *Characterization of the International Humic Substances Society Standard and Reference Fulvic and Humic Acids by Solution State Carbon-13 (¹³C) and Hydrogen-1 (¹H) Nuclear Magnetic Resonance Spectrometry*; U.S. Geological Survey: Denver, CO, 1989.
57. Boyle, E. S.; Guerriero, N.; Thiallet, A.; Del Vecchio, R.; Blough, N. V.; Optical Properties of Humic Substances and CDOM: Relation to Structure. *Environmental Science & Technology* **2009**, 43, (7), 2262-2268.
58. Del Vecchio, R.; Blough, N. V.; On the origin of the optical properties of humic substances. *Environmental Science & Technology* **2004**, 38, (14), 3885-3891.
59. Korshin, G. V.; Li, C. W.; Benjamin, M. M.; Monitoring the properties of natural organic matter through UV spectroscopy: A consistent theory. *Water Research* **1997**, 31, (7), 1787-1795.
60. Wert, E. C.; Rosario-Ortiz, F. L.; Snyder, S. A.; Using Ultraviolet Absorbance and Color To Assess Pharmaceutical Oxidation during Ozonation of Wastewater. *Environmental Science & Technology* **2009**, 43, (13), 4858-4863.
61. Li, C. W.; Benjamin, M. M.; Korshin, G. V.; Use of UV spectroscopy to characterize the reaction between NOM and free chlorine. *Environmental Science & Technology* **2000**, 34, (12), 2570-2575.
62. von Sonntag, C.; von Gunten, U., *Chemistry of Ozone in Water and Wastewater Treatment - From Basic Principles to Applications*. IWA Publishing: 2012; p 320.
63. Criegee, R.; Mechanism of ozonolysis. *Angewandte Chemie-International Edition in English* **1975**, 14, (11), 745-752.
64. Gulkowska, A.; Sander, M.; Hollender, J.; Krauss, M.; Covalent binding of sulfamethazine to natural and synthetic humic acids: assessing laccase catalysis and covalent bond stability. *Environmental Science & Technology* **2013**, 47, (13), 6916-6924.
65. Wardman, P.; Reduction potentials of one-electron couples involving free radicals in aqueous solution. *Journal of Physical and Chemical Reference Data* **1989**, 18, (4), 1637-1755.
66. Reale, S.; Di Tullio, A.; Spreti, N.; De Angelis, F.; Mass spectrometry in the biosynthetic and structural investigation of lignins. *Mass Spectrometry Reviews* **2004**, 23, (2), 87-126.
67. Ravacha, C.; The reactions of chlorine dioxide with aquatic organic materials and their health effects. *Water Research* **1984**, 18, (11), 1329-1341.
68. Wajon, J. E.; Rosenblatt, D. H.; Burrows, E. P.; Oxidation of phenol and hydroquinone by chlorine dioxide. *Environmental Science & Technology* **1982**, 16, (7), 396-402.
69. Lind, J.; Shen, X.; Eriksen, T. E.; Merenyi, G.; The one-electron reduction potential of 4-substituted phenoxyl radicals in water. *Journal of the American Chemical Society* **1990**, 112, (2), 479-482.
70. Li, C.; Hoffman, M. Z.; One-electron redox potentials of phenols in aqueous solution. *Journal of Physical Chemistry B* **1999**, 103, (32), 6653-6656.

- 632 71. *CRC Handbook of Chemistry and Physics*. 70th ed.; CRC Press, Inc.: Boca Raton,
633 Florida, 1989.
- 634 72. Rebenne, L. M.; Gonzalez, A. C.; Olson, T. M.; Aqueous chlorination kinetics
635 and mechanism of substituted dihydroxybenzenes. *Environmental Science & Technology*
636 **1996**, 30, (7), 2235-2242.

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